

to understand the chemical behavior and properties of a specific organometallic complex. However, despite the vast information provided by crystal structures, it cannot always indicate how the complex will behave in solution state in the presence of other coordinating molecules. Therefore the use of various spectroscopic methods such as Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (IR) *etc.* in conjunction with crystallography allows a much better understanding into the chemical properties of a complex.

Our interest in homogenous catalysis, in particular, the Rhodium Monsanto process [1] which produces several million tons of acetic acid per annum has allowed us to explore both spectroscopic and crystallographic methods to better understand the catalytic cycle. Selecting catalysts which have been altered with various ligands with different stereo-electronic properties, it is possible to control the selectivities and rates of the catalytic reaction [2-4].

The precursor effect of the methanol carbonylation catalytic cycle was studied with various model complexes of the type $[\text{Rh}(\text{L},\text{L}'\text{-Bid})(\text{CO})(\text{PR}_3)]$ ($\text{L},\text{L}'\text{-Bid}$ = mono anionic bidentate ligand; PR_3 = alicyclic and aryl tertiary phosphine compounds). Crystallographic comparisons of the complexes were correlated with spectroscopic studies to determine the solid state and solution effects introduced by the selective variation in the substituents on the phosphorous atom [5-6].

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Keywords: crystallography, spectroscopy, rhodium

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Structural Origin of Ferromagnetism in Mn- and Co-doped Y_2O_3 Nanocrystals

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Long-range-order and short-range-order structures in ferromagnetic Mn- and Co-doped Y_2O_3 nanocrystals prepared by a thermal decomposition method have been probed using x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) techniques, respectively. These diluted magnetic oxides (DMO) are high-k dielectrics and exhibit ferromagnetism at room temperature. Our EXAFS results indicate that oxygen vacancies are present around the Mn and Co dopant atoms in the Y_2O_3 DMO host. To investigate the correlation between ferromagnetism and oxygen vacancies, the as-made sample were alternately annealed in oxygen and forming gas at a moderate annealing temperature. The EXAFS data reveals that the average number of oxygen vacancies surrounding magnetic dopant atoms is increased by oxygen annealing and decreased by forming-gas annealing. The XANES results also demonstrate consistent valency variations. Without appreciable changes in particle size, the saturation magnetization was found to increase with oxygen-vacancy concentration in these DMO samples. Our results strongly support the bound magnetic polaron model for ferromagnetism in these DMO nanocrystals.

Keywords: ferromagnetic, high-k, exafs

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The X-ray Extended Range Technique for high accuracy XAS for comparison and improvement to theoretical modeling

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The x-ray atomic form factor is the fundamental parameter describing the interaction of x rays with matter. Accurate values of the mass attenuation coefficient and hence of the dielectric function are vital for many areas of x-ray science. A wide range of atomic, molecular, and solid-state features can be calculated given accurate values of x-ray atomic form factors of the constituent elements. However, large discrepancies between different theoretical calculations exist, and are largest in the important absorption edge regions [1,2]. We have developed the X-ray Extended Range Technique (XERT) to measure x-ray mass attenuation coefficients to accuracies as low as 0.02% [3,4,5]. From these measurements the form factors are derived and used help improve theoretical approaches. Two recent reviews have discussed experimental details [6,7].

We present measurements of the x-ray mass attenuation coefficients of zinc, selenium and zinc selenide are measured between 7.2 keV and 15.2 keV with an absolute accuracy of 0.044% - 0.197% and a relative accuracy down to 0.006%, making this the most accurate determination of any attenuation coefficient on a bending-magnet beamline [8]. The measurements invite improvements in theoretical calculations of mass attenuation coefficients. Comparison between zinc, selenium and zinc selenide measurements tests the effect of structure and bonding, and the sum rule in theoretical calculations of the mass attenuation coefficient. In particular theoretical calculations of XAFS and XANES [9] are compared to the measurements.

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Modulation excitation spectroscopy adapted to Crystallography

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Modulation excitation spectroscopy is a powerful and well established technique to investigate the dynamic behavior of chemical

and physical systems [1, 2]. An external stimulus is applied to the system, by periodically varying a parameter affecting it (for example concentration, pH, light flux, temperature or pressure). The response of the system, which is also periodic, is first averaged into one period, then analyzed offline by means of phase-sensitive detection, i.e. by separating the signals of the different frequency terms. A high signal-to-noise ratio is gained by the averaging procedure and the phase-sensitive detection, recovering small signals buried under large ambient noise, besides achieving high time-resolution for kinetic studies [1].

We conceived the application of this technique to Crystallography for two main reasons: to select contributions to the diffraction pattern arising from specific groups of atoms in the crystal cell and to achieve a time-dependent characterization of the crystallized system.

To this aim, we developed a theory to explain the diffraction response of a crystal subjected to a periodically varying external perturbation, where the effect of the variation of different structural parameters on the diffraction intensity is accounted for [3]. We showed that the interference contribution of the substructure composed by the atoms actively responding to the stimulus may be separated by analyzing the diffraction signal at a frequency which is double with respect to that of the external stimulus. This new technique has been called Modulation Enhanced Diffraction (MED).

Experiments to verify the MED potentialities have been first simulated and then carried out at synchrotron sources. The experiments carried out on powder samples, by periodically varying the X-ray beam energy or the pressure exerted by a gas on the sample, will be described.

The data analysis involves two steps: first the phase sensitive detection is applied to a set of diffraction patterns of one modulation cycle to obtain a demodulated pattern, then a phasing procedure is applied to it.

A special procedure, making use of the Patterson deconvolution technique [4], has been developed and successfully used to phase the demodulated diffraction patterns and obtain the substructure of the active moiety.

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Influence of defects on the polarization dependent DAFS of Rutile TiO₂

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The structural defects of annealed rutile (TiO₂) samples have been studied by means of polarization dependent *Diffraction Anomalous Fine Structure* (DAFS) also known as *Anisotropic Anomalous Scattering* (AAS). The investigations of the 'forbidden' 001 and allowed 111 reflection (see Fig. 1) extend the results for the undisturbed rutile structure, space group (136) P4₂/mnm, obtained from AAS by Kirfel and Petcov [1] and from *X-ray Absorption Fine Structure* (XAFS)

analysis (e.g. [2]).

Further, the signature of defects (see e.g. [3]) occurring after thermal treatment at 800°C temperature in a vacuum of about 10⁻⁶ mbar is discussed. An interpretation of changes in the DAFS signal due to electronic transitions into altered unoccupied states is attempted by means of FDM [4] simulations. The considered defects include an oxygen vacancy and a Ti interstitial structure in 2 x 2 x 3 supercells, which in advance have been relaxed using density functional theory. Experiments were performed in the vicinity of the Ti-K absorption edge at DESY/HASYLAB beamlines W1 and E2 on a series of 10 x 10 x 1 mm³ single crystal wafers from Crystec GmbH Berlin.

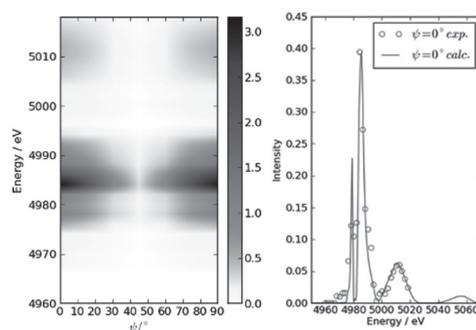


Fig. 1.: Polarization dependent DAFS of 001 forbidden reflection of rutile for σ - π channel (left) and comparison to FDMNES [4] calculation (right).

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Crystal structure and local atomic order in nanostructured La_{0.6}Sr_{0.4}CoO_{3- δ}

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Mixed ionic-electronic conducting oxides (MIECs) based on transition metal oxides have important application as cathodes in solid oxide fuel cells (SOFCs). The high working temperature of the SOFCs (900 to 1000°C) requires expensive materials to be used as collectors and interconnectors. Start-up and shut-down also reduces the SOFC's life span due to thermal stresses. So, a great effort is dedicated to the research and development of new cathode materials that exhibit high electro catalytic activity and high ionic conductivity at lower temperature (500-700°C) to be applicable to intermediate temperature SOFCs (IT-SOFCs).

La_{0.6}Sr_{0.4}CoO_{3- δ} (LSC) is one of the best candidates for IT-SOFC cathodes. It exhibits the perovskite-type structure ABO_{3- δ} , where Sr replaces La in the A site, thus introducing oxygen vacancies, which are the responsible for the ionic conduction.

Recently, we have demonstrated that nanostructured LSC cathodes exhibit better electric properties than microstructured ones (area specific resistance, ASR=0.084 and 0.154 ohm cm², respectively). We showed that this high performance is related to the enhanced ionic diffusivity of the nanostructured cathodes [1].